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Note

Preparation of 1-(azidoaryl)amido- and 1-(azidoaryl)thio-1-deoxy-D-fructose analogs

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Increased interest in the mechanism of sugar transporters has led to use of photoreactive cross-linking reagents such as the light-sensitive *N*-hydroxysuccinimide ester of 4-azido-2-hydroxybenzoic acid[1–5] (**2**), the *N*-hydroxysuccinimide ester of 4-azidobenzoic acid[6–8], and 4-fluoro-3-nitrophenyl azide[9,10] (**3**) for introducing photoreactive atoms into some hexoses. Extension of photoaffinity labeling to D-fructose (**1**) has resulted in the present synthesis of 1-(4-azido-2-hydrobenzamido)-1-deoxy-β-D-fructose (**7**) and 1-(4-azido-2-nitrophenyl)thio-1-deoxy-D-fructose (**11**) for use as potential photoprobes to study mechanism for transport of D-fructose (**1**) in corn endosperm.

Previous reports have described the synthesis of isopropylidene-blocked *N*-fructopyranosylamino acid esters[11], and deblocked *N*-fructofuranosyl-[12] and fructopyranosylamino acid esters[12,13–15].

RESULTS AND DISCUSSION

Catalytic reduction of 1-azido-1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose[16] (**4**) with 5% Pd-C in ethanol gave syrupy 1-amino-1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**5**), whose structure was assigned from its elemental analysis and ^{1}H-n.m.r. spectral data. A light-sensitive reaction was conducted in low-actinic glassware, whereupon 1-(4-azido-2-hydroxybenzamido)-1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**6**) was obtained by acylation of **5** with **2** in *N*,*N*-dimethylformamide (DMF) for 48 h at 25°. Compound **6** was isolated by column chromatography in 87% yield. Elemental analysis agreed with the formula $C_{19}H_{24}N_4O_7$ for **6**, which was supported by mass spectrometry by a molecular ion ($M^+ + 1$) at *m/z* 421. The ^{1}H-n.m.r. spectral data for **6** were consistent with assigned structure.

Deblocking of **6** was accomplished in 5 h with acidic cation-exchange

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TABLE I

CARBON-13 CHEMICAL SHIFTS[a] AT 75.4 MHz FOR SOLUTIONS OF 1-*S*- AND 1-*N*-SUBSTITUTED D-FRUCTOSE ANALOGS

Carbon	D-*Fructopyranose ring-forms*[b]		D-*Fructofuranose ring-forms*[c]	
	S-*Substituted*	N-*Substituted*	S-*Substituted*	N-*Substituted*
C-1	40.6	45.8 (65.6)[d]	49.5	44.4 (64.7)[d]
C-2	98.9	98.8 (99.1)	101.2	101.2 (102.8)
C-3	70.6	69.8 (69.3)	78.6	76.9 (77.5)
C-4	70.3	69.7 (71.1)	74.9	74.4 (76.3)
C-5	69.6	69.7 (70.4)	81.5	80.8 (82.1)
C-6	64.4	64.2 (64.6)	62.7	62.4 (63.7)

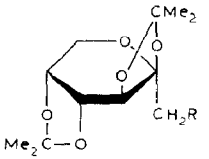
[a]Carbon-13 signals, p.p.m. from Me_4Si. [b]High-intensity signals for fructopyranose ring-forms. [c]Low-intensity signals for fructofuranose ring-forms. [d]Reported refs. 12, 13, and 14.

resin[16–18] in 40% methanol–water at 48–50° to give 1-(4-azido-2-hydroxybenzamido)-1-deoxy-β-D-fructose (**7**); it melted with decomposition at 80°, and was strongly reducing toward alkaline 2,6-dichloroindophenol, which is indicative of Amadori rearrangement compounds. Compound **7** was stable for 3–4 weeks at 25°; it may be stored over Drierite for several months at −12°.

The ^{1}H-n.m.r. spectrum of **7** was complicated by the presence of protons from pyranose and furanose ring-forms[12–14,19–22] and it was only partially interpreted. ^{13}C-N.m.r. spectroscopy showed that compound **7** exists mainly in the β-pyranose ring-form; signals of a small proportion of furanose ring-forms were also observed (Table I).

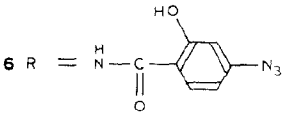
Chapman and Owen[23] described the reaction of potassium thiolacetate with *p*-toluene- and methane-sulfonic esters as a method for preparation of thio sugars. Subsequently, Baker[24] demonstrated nucleophilic displacement of a *p*-toluenesulfonic ester group in 2,3:4,5 di-*O*-isopropylidene-1-*O*-*p*-tolylsulfonyl-D-fructose with sodium ethanethiolate in the synthesis of 1-*S*-ethyl-1-thio-D-fructose.

As 1-*S*-substituted analogs are stable at 25° and more resistant to acid hydrolysis than compound **7**; this work was extended to the synthesis of a 1-(arylazido)thio-D-fructose analog (**11**). Nucleophilic displacement of a 1-triflate group from 2,3:4,5-di-*O*-isopropylidene-1-*O*-(trifluoromethanesulfonyl)-β-D-fructopyranose[18] (**8**), by potassium thiolacetate[23] (**14**) gave 1-*S*-acetyl-2,3:4,5-di-*O*-isopropylidene-1-thio-β-D-fructopyranose (**9**); base hydrolysis with NaOMe gave a sodium thiolate salt[10] **12**. A light-sensitive reaction was conducted without isolated **12**, by treating 4-fluoro-3-nitrophenyl azide (**3**) directly with compound **12** at 25°. 1-(4-Azido-2-nitrophenyl)thio-1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**10**) was obtained in 68% yield along with bis(1-deoxy-2,3:4,5-di-*O*-isopropylidene-D-fructopyranos-1-yl) disulfide (**13**) in 4.4% yield. Sodium methoxide hydrolyzed the thioacetate to give the free thiol, which readily undergoes oxidative dimerization whereby a disulfide dimer (**13**) was formed[25].



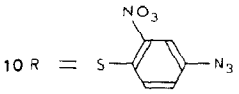
4 R = N_3

5 R = NH_2

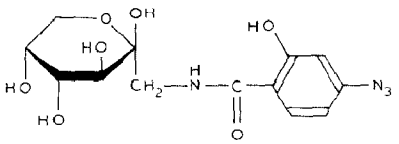


8 R = OSO_2CF_3

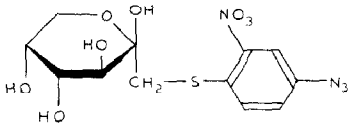
9 R = $SCOCH_3$



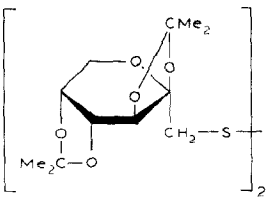
12 R = S^-Na^+



7



11



13

Deacetonation of **10** with 9:1 (v/v) trifluoroacetic acid[26] gave 1-(4-azido-2-nitrophenyl)thio-1-deoxy-D-fructose (**11**) in 62.5% yield.

The ^{1}H-n.m.r. spectrum for compound **11** was also complicated by signals from other tautomeric ring-forms[12–14,19–22]; and it was only partially interpreted. The ^{13}C spectrum showed that **11** was mainly the β-pyranose tautomer, with a small proportion of furanose tautomers also present (Table I). The ^{13}C spectra also demonstrated equilibria between pyranose and furanose ring-forms for compounds **7** and **11** in D_2O solution.

EXPERIMENTAL

General methods. — Commercial D-fructose (**1** Fisher Scientific Co. Fair Lawn, NJ), the *N*-hydroxysuccinimide ester of 4-azido-2-hydroxybenzoic acid (**2**), 4-fluoro-3-nitrophenyl azide (**3**, Pierce Chemical Co., Rockford, IL), palladium (5%) on charcoal (Matheson Coleman and Bell, Norwood, OH), trifluoromethanesulfonic anhydride, potassium thiolacetate (Aldrich), Bio-Rd Dowex 50W-X8 (Bio-Rad Laboratories, Richmond, CA), and reagent-grade 1,2-dichloromethane, methanol, acetone, and *N*,*N*-dimethylformamide were used.

Reactions were monitored by t.l.c. Purity of the products was established by dry Silica Gel G column chromatography, by t.l.c., and by elemental analyses. T.l.c. was conducted on 0.25-mm EM Reagent Silica Gel G (Brinkman Instrument,

Inc.) with air-dried plates. The spots were detected by spraying with 5% ethanolic H_2SO_4 acid and charring. Dry column chromatography on Silica Gel G was performed with 80% (v/v) hexane–ethyl EtOAc and 3:1 (v/v) hexane–EtOAc for the substituted compounds. T.l.c. and dry column chromatography were performed with 23:2 (v/v) butanone–water azeotrope–abs. EtOH for unsubstituted compounds. Specific rotations were recorded with a Perkin–Elmer Model 241 polarimeter. I.r. spectra were obtained with KBr pellets (3.0 $mg.g^{-1}$ KBr) or as thin films with a Beckman IR-33 instrument. Mass spectrometry (m.s.) and tandem mass spectrometry (m.s.–m.s.) were performed with a Finnigan 4535/TS Q quadrupole mass spectrometer equipment with a DEP probe. The ^1H- and ^{13}C-n.m.r. spectra were recorded in 5-mm tubes with a Bruker WH-300 WB Fourier-transform n.m.r. spectrometer at 300 and 74.5 MHz. Sweep widths of 221 p.p.m. with 8192 datapoints were used to give chemical shifts accurate to within ±2 Hz (±0.05 p.p.m.). A memory size (8192 addresses) set the data-acquisition time at 0.46 sec. Proton noise-decoupled, DEPT spectra were obtained to assist in signal assignments. Melting points, measured in capillary tubes, are not corrected. Microchemical analyses were performed by Galbraith Laboratories, Inc.

*1-Azido-1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-*D*-fructopyranose* (**4**). — Compound **4** (28 g), prepared by the procedure of Card *et al.*[16], was purified by passing through a column of dry silica gel and eluting with 80% hexane–EtOH. Fractions were collected and combined to yield 18.1 g of **4** (88.3%, noncrystalline, solidified); m.p. 56–58.5°, $[\alpha]_D^{25}$ −88.6° (*c* 1, $CHCl_3$); reported[16] m.p. 55.5–60°, $[\alpha]_D^{20}$ −88.9°.

*1-Amino-1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-*D*-fructopyranose* (**5**). — The azido group or compound **4** (12 g) was reduced in the presence of 5% palladium on carbon catalyst (0.5 g) in abs. EtOH at 25° with an initial hydrogen pressure of 50 $lb.in^{-2}$. The catalyst was removed by filtration and solvent was removed under diminished pressure to afford **5** as a noncrystalline mixture (10.3 g). Compound **5** was purified by dry Silica Gel G column chromatography eluting with 80% EtOAc–MeOH; yield 9.98 g (91%); $[\alpha]_D^{25}$ −30.7° (*c* 1, $CHCl_3$); ^1H-n.m.r. ($CDCl_3$): δ 2.94 (d, H-1, *J* 13.7 Hz). 2.85 (d, H-1′, *J* 13.8 Hz), 4.16 (d, H-3, *J* 2.5 Hz), 4.57 (dd, H-4, *J* 2.4, 7.9 Hz), 4.23 (dd, H-5, *J* 1.4, 7.9 Hz), 3.88 (dd, H-6, *J* 1.9, 13.9 Hz), 3.75 (dd, H-6′, *J* 7.0, 14.0 Hz), 1.77 (bs, NH), 1.35 (s, 3 H), 1.37 (s, 3 H), and 1.47 (s, 3 H), 1.53 (s, 3 H).

Anal. Calc. for $C_{12}H_{21}NO_5$: C, 55.60; H, 8.13; N, 5.40. Found: C, 55.40; H, 8.12; N, 5.47.

*1-(4-Azido-2-hydroxybenzamido)-1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-*D*-fructopyranose* (**6**). — Compound **5** (0.94 g, 3.6 mmol) was dissolved in DMF (15 mL) and the *N*-hydroxysuccinimide ester of 4-azido-2-hydroxybenzoic acid (2, 1.0 g, 3.7 mmol) was added. The reaction was allowed to proceed for 48 h at 25° with constant stirring. The DMF was evaporated under diminished pressure, whereupon t.l.c. disclosed unaltered **2** plus compound **6**. The syrup (2.7 g) was passed through a column of dry Silica Gel G that was eluted with 2:1 hexane–EtOAc. Fractions

were collected and combined to yield 1.3 g (87%) of pure, noncrystalline **6**; $[\alpha]_D^{25}$ −13.7° (*c* 0.6, $CHCl_3$); ^{1}H-n.m.r. data (chloroform-*d*): δ 3.65 (d, H-1, *J* 4.8 Hz), 3.88 (d, H-1′), 4.58 (d, H-3, *J* 2.6 Hz), 4.61 (d, H-4, *J* 2.6 Hz), 4.32 (d, H-5, *J* 2.6 Hz), 3.74 (dd, H-6, *J* 13.1 Hz), 3.86 (m, H-6′), 6.86 (NH), 1.34 (s, 3 H), 1.38 (s, 3 H), 1.41 (s, 3 H), 1.53 (s, 3 H), 6.61 (ar-d, H-3, *J* 2.2 Hz), 6.45 (ar-d, H-5, *J* 8.5 Hz), and 7.38 (ar-d, H-6, *J* 8.6 Hz); ν_{max}^{film} 3380 (H-bonded OH, broad), 3000–2950 cm^{-1} (CH_2, CH_3), 2110 (N_3), 1650 (NH-C:O, broad), and 1600 cm^{-1} (C=C); *m/z* 421 ($M^+ + 1$).

Anal. Calc. for $C_{19}H_{24}N_4O_7$: C, 54.28; H, 5.75; N, 13.33. Found: C, 54.37; H, 5.91; N, 13.43.

*1-(4-Azido-2-hydroxybenzamido)-1-deoxy-β-*D*-fructose* (**7**). — Compound **6** (1 g, 3.1 mmol) was treated with acidic cation-exchange resin (10.0 g) in 40% MeOH–water (25 mL) at 48–50° with continuous stirring for 5 h. Ion-exchange resin was removed by filtration and the filtrate was poured into water and extracted twice with $CHCl_3$ and twice with anhydrous ether. T.l.c. disclosed one major component with traces of impurities in the aq. extract. The latter was evaporated under vacuum at 35° to 15 mL and then lyophilized to afford **7** as a white solid (0.240 g, 21%); it crystallized from cold water and melted with decomposition at 80°. Unaltered **6** (0.8 g), recovered from the $CHCl_3$ and ether extractions, was recycled through the hydrolytic process, thus resulting in a 41% overall yield for **7**; ν_{max}^{KBr} 3680–3000 centered at 3340 (OH, very broad), 1600 (C=C), 1650 (NH-C=O), and 2110 cm^{-1} (N_3); ^{1}H-n.m.r. (D_2O): δ <6.00 complex (β-pyranose and β-D-furanose)[12–14]; 6.56 (ar-H-3, NH), 6.49 (d, ar-H-5, *J* 8.6 Hz), and 7.63 (d, ar-H-6, *J* 8.6 Hz); ^{13}C-n.m.r. ($CDCl_3$): aromatic ring-carbon signals, 159.5 (C-1), 146.1 (C-2), 131.1 (C-3), 111.4 (C-4), 107.6 (C-5), 107.6 (C-6), and 170.1 (C=O) p.p.m.; see also Table I.

Anal. Calc. for $C_{13}H_{16}N_4O_7$: C, 45.88; H, 4.74; N, 16.47. Found: C, 45.66; H, 4.94; N, 16.24.

*2,3:4,5-Di-O-isopropylidene-1-O-(trifluoromethanesulfonyl)-β-*D*-fructopyranose* (**8**). — Compound **8** was prepared by the procedure of Card *et al.*[16] and purified by passing it through a column of dry Silica Gel G that was eluted with 80% (v/v) hexane–EtOAc.

*1-S-Acetyl-2,3:4,5-di-O-isopropylidene-1-thio-β-*D*-fructopyranose* (**9**). — A solution of **8** (21 g, 53.5 mmol) in dry acetone (150 mL) at −15° was added to a suspension of KSAc (**14**, 7.1 g, 62.3 mmol, slight excess) in dry acetone (150 mL) at −15°. The mixture was kept overnight (20 h) with mechanical stirring at 25°. The potassium triflate and excess KSAc were removed by filtration; whereupon, the solids were washed with $CHCl_3$; combined filtrates were evaporated under diminished pressure and the residue re-dissolved in $CHCl_3$ (150 mL); $CHCl_3$ solution was washed with ≤0.1M HCl and water three times each, and this solution was dried over Na_2SO_4 and evaporated under diminished pressure. T.l.c. disclosed compound **9** and unreacted 1-triflic ester (**8**) in the $CHCl_3$ extract; the syrup (27.2 g) was passed through a column of dry Silica Gel G and eluted with 3:1 (v/v) hexane–

EtOAc. Fractions were collected and combined to yield 9.7 g (76%) of pure noncrystalline **9**; however, **9** solidified upon standing; m.p. 49.5–52°; $[\alpha]_D^{25}$ −2.9° (*c* 1, $CHCl_3$): ^{1}H-n.m.r. ($CDCl_3$): δ 3.29 (1/2 AB, H-1, *J* 13.7 Hz), 3.23 (1/2 AB, H-1′, *J* 13.8 Hz), 4.10 (m, H-3), 4.46 (q, H-4, *J* 2.4, 2.44 Hz), 4.10 (m, H-5), 3.74 (AB, H-6, *J* 11.2, *J* 1.9, *J* 1.8 Hz), 3.61 (AB, H-6, *J* 12.7 Hz), 2.23 (s, $COCH_3$), 1.23 (s, 3 H), 1.29 (s, 3 H), 1.38 (s, 3 H), 1.40 (s, 3 H); ν_{max}^{film} 1695, sh at 1715 cm^{-1} ($SCOCH_3$ thiol ester); *m/z* 318 (M), 89 ($C_7H_5N_4O_2S$), 229 ($C_{11}H_{17}O_5$).

Anal. Calc. for $C_{14}H_{22}O_6S$: C, 52.81; H, 6.96; S, 10.07. Found: C, 53.04; H, 7.16; S, 11.01.

*1-(4-Azido-2-nitrophenyl)thio-1-deoxy-2,3:4,5-di-O-isopropylidene-β-*D*-fructopyranose* (**10**). — Solutions of **9** (3.8 g, 12 mmol) in dry MeOH (10 mL) and a solution of NaOMe (0.72 g, 13.4 mmol) in dry MeOH (10 mL) were combined and kept for 5 min at 25°; without isolation, the sodium thiolate salt **12** was condensed directly with 4-fluoro-3-nitrophenyl azide (**3**, 2.0 g, 11 mmol). The mixture was kept for 30 min at 25°. The residue was redissolved in DMF (50 mL), after removal of MeOH under nitrogen. This solution was kept in the dark for 3.5 h at 25°, undissolved solids were removed by filtration, and solvent was evaporated under diminished pressure. T.l.c. disclosed compound **10**, plus unaltered **3**, **9** and bis(1-deoxy-2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranos-1-yl) disulfide (**13**). The syrup (6.1 g) was passed through a column of dry Silica Gel G that was eluted with 3:1 (v/v) hexane–EtOAc. The mixture (4.4 g) was rechromatographed to yield 3.58 g (68%) of pure, noncrystalline **10**, plus 0.3 g (4.4%) of pure noncrystalline **13**; $[\alpha]_D^{25}$ −83° (*c* 1, $CHCl_3$), ^{1}H-n.m.r. ($CDCl_3$): δ 3.53 (1/2 AB, H-1, *J* 14.3 Hz), 3.23 (1/2 AB, H-1′, *J* 14.3 Hz), 4.35 (d, H-3, *J* 2.6 Hz), 4.60 (q, H-4, *J* 2.6, 2.6 Hz), 4.23 (d, H-5), 3.93 (1/2 AB, H-6, *J* 1.8, 1.9, 11.1 Hz), 3.78 (1/2 AB, H-6′, *J* 12.8 Hz), 1.29 (s, 3 H), 1.32 (s, 3 H), 1.47 (s, 3 H), 1.47 (s, 3 H), 7.16 (ar-q, H-3, *J* 2.5, 2.6 Hz), 7.75 (ar-m, H-5), and 7.75 (ar-m, H-6); ν_{max}^{film} 2110 (N_3) and 1600 cm^{-1} (C=C); *m/z* 438 (M^+), 209 ($C_7H_5N_4O_2S$), and 229 ($C_{11}H_{17}O_5$).

Anal. Calc. for $C_{18}H_{22}N_4O_7S$: C, 49.31; H, 5.06; N, 12.78; S, 13.63. Found: C, 49.56; H, 5.19; N, 12.52; S, 13.49.

*1-(4-Azido-2-nitrophenyl)thio-1-deoxy-*D*-fructose* (**11**). — Acid hydrolysis of isopropylidene groups were accomplished by the method of Marsh and Goodman[26]; however, t.l.c. disclosed some degradation products in reaction residue and therefore, **11** was purified by passing it through a column of dry Silica Gel G eluted with 80% (v/v) toluene–abs. EtOH. Fractions were collected and combined, evaporated at 35°, and the residue was redissolved in water (15 mL) and then lyophilized to give a red solid; yield 0.560 g (62.5%); m.p. (dec.) 60°; ^{1}H-n.m.r. (D_2O): δ <6.00 (complex)[12–14], 7.71 (ar-H-3), 7.53 (ar-H-5), 7.25 (ar-H-6); ^{13}C-n.m.r. data ($CDCl_3$): (aromatic ring-carbon signals) δ 147.3 (C-1), 138.4 (C-2), 130.3 (C-3), 132.3 (C-4), 125.5 (C-5), and 116.6 (C-6) p.p.m.; see also Table I.

Anal. Calc. for $C_{12}H_{14}N_4O_7S$: C, 40.22; H, 3.94; N, 15.64; S, 8.95. Found: C, 40.33; H, 3.86; N, 15.38; S, 8.88.

*Bis(1-deoxy-2,3:4,5-di-*O*-isopropylidene-*D*-fructopyranos-1-yl) disulfide* (**13**).

— Acetic ester group removed by NaOMe to give the free thiol; compound **13** was formed as a by-product in the mixture; $[\alpha]_D^{25}$ −54.1° (*c* 1, $CHCl_3$); ^{1}H-n.m.r. ($CDCl_3$): δ 3.34 (1/2 AB, H-1, *J* 14.0 Hz), 3.09 (1/2 AB, H-1′, *J* 13.8 Hz), 4.26 (d, H-3, *J* 2.6 Hz), 4.55 (q, H-4, *J* 2.6, 2.6 Hz), 4.17 (q, H-5, *J* 2.2, 1.2 Hz), 3.82 (1/2 AB, H-6, *J* 12.6, 1.8, 1.9 Hz), 3.67 (1/2 AB, H-6′, *J* 11.1 Hz), 1.29 (s, 3 H), 1.38 (s, 3 H, 1.44 (s, 3 H), 1.47 (d, 3 H); *m/z* 550 (M^+).

Anal. Calc. for $C_{24}H_{38}O_{10}S_2$: C, 52.35; H, 6.96; S, 11.65. Found: C, 52.42; H, 7.22; S, 11.88.

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